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Examinations on 2.5 V $Li[Li_{1/3}Ti_{5/3}]O_4/Li[Li_{0.1}Al_{0.1}Mn_{1.8}]O_4$ cells at −10, 25, and 55 °C for the first-generation 12 V lead-free batteries

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ABSTRACT

Electrochemical behaviors of 2.5 V $Li[Li_{1/3}Ti_{5/3}]O_4$ (LTO)/$Li[Li_{0.1}Al_{0.1}Mn_{1.8}]O_4$ (LAMO) cells for the first-generation 12 V lead-free battery were examined at −10, 25, and 55 °C. The LTO/LAMO cells showed the same rechargeable capacity in temperature ranging from −10 to 55 °C when the cells were examined at 0.5 mA cm^{-2} in cell potential ranging from 0 to 3.0 V. Capacity fading after 250 cycles was negligibly small at −10 °C. Rechargeable capacities, however, faded 5% at 25 °C and 15% at 55 °C after 250 cycles. In the discharged LTO/LAMO cell after 250 cycles at 55 °C, the state of charge (SOC) of the positive electrode was 16% while SOC of the negative electrode was 0%, indicated that the capacity fading was due to an imbalance in SOC between the positive and negative electrodes. To understand the progress of an imbalance in SOC, the LTO/LAMO cell with a lithium auxiliary electrode was fabricated and examined at 55 °C for 400 cycles, and the possible origin of capacity fading was discussed.

1. Introduction

In previous papers [1–4], we have proposed the 12 V lead-free batteries for high-power long-life applications. The first-generation 12 V lead-free batteries consist of lithium titanium oxide (LTO), so-called zero-strain insertion material of $Li[Li_{1/3}Ti_{5/3}]O_4$ [5–9], and lithium manganese oxides (LMO) or their derivatives [10], specifically lithium aluminum manganese oxide (LAMO) of $Li[Li_{0.1}Al_{0.1}Mn_{1.8}]O_4$ [11]. The operating cell potential of the LTO/LAMO cell is ca. 2.5 V, so that the 12 V batteries can be made connecting five cells in series. According to previous reports on LTO and LMO [12–18], the cells show good cycleability [4,13–15], rate capability [13,15–17], and stability associated with safety [3,14,17,18]. Therefore, the first-generation 12 V batteries seem to have several advantages over the 12 V lead-acid batteries in terms of energy density and cycleability. For automobile and stationary applications of the 12 V batteries [19,20], low and high temperature examinations are required because the batteries are exposed to such cold and hot environments. In recent years, automobile applications include idling stop cars, hybrid electric vehicles, plug-in hybrid electric vehicles, and pure electric vehicles. In such applications, high output power for a short period of time is required for starting or accelerating, and high input power is also required for breaking and consequently for extending mileage. In this paper, the results on the single cell examinations of LTO/LAMO cells at −10, 25, and 55 °C are described and the capacity fading is discussed in terms of the imbalance in state-of-charge (SOC) between the positive and negative electrodes.

2. Experimental

LTO and LAMO used in this study were the same as described in a previous paper [3]. The electrochemical cell consisted of positive and negative electrodes separated by two sheets of polypropylene microporous membrane (40 μm thick in dry) or polybutylene terephthalate (PBT) non-woven cloth (55 μm thick in dry). The PBT separators were dried under vacuum at 100 °C for 2 h before use. These materials were placed in a cavity of a container. The container consisted of two insulated stainless steel plates (70 mm × 65 mm, 5 mm thick.) separated by a Teflon spacer (2 mm thick.) in which a 25 mm × 35 mm window was made. In preparing the electrodes, black viscous slurry consisted of 88 weight percent (wt%) of LTO or LAMO, 6 wt% acetylene black, and 6 wt% polyvinylidene fluoride (PVdF) dispersed in *N*-methyl-2-pyrrolidone (NMP) was cast onto aluminum foil for the LAMO and LTO electrodes. The electrodes were dried at room temperature and then heated at 60 °C for 1 h under vacuum to remove NMP, and finally they were dried under vacuum at 150 °C overnight. After drying, the electrodes were punched out into a disk having 16.0 mm in diameter, i.e., 2 cm^2 in apparent area. A lithium electrode was prepared by pressing lithium metal onto a stainless steel plate. The electrolyte was 1 M $LiPF_6$ dissolved in ethylene carbonate (EC)/dimethyl carbonate (DMC) (3/7 by volume) solution obtained from Kishida Chemical Co. Ltd., Japan. An electrochemical cell with three-electrode configura-

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tion was also fabricated and examined [3]. A lithium auxiliary electrode was placed between two sheets of separators and around the positive and negative electrodes, and the potentials of positive and negative electrodes were monitored with respect to a lithium electrode. All materials except the electrolyte and lithium metal were dried under vacuum at 40 °C for 2 h to avoid possible contamination of water. The cells were fabricated in an argon-filled glove box. Other sets of experimental conditions are described in Section 3.

3. Results and discussion

One of the requirements for the 12 V batteries is high power output and also input for a short period of time for automobile applications. Fig. 1 shows the pulse charge and discharge curves of the LTO/LAMO cell operated at 15.3 mA cm^{-2} for 5 s current on and 25 s off. The current corresponds to 0.68 A g^{-1} based on the weight of LAMO and 1 A g^{-1} based on LTO. The continuous charge and discharge curves of the cell operated at 0.5 mA cm^{-2} are also shown. The separator used is two-ply polypropylene microporous membrane. Three dotted lines from the bottom to top in Fig. 1 are 7.2, 10.2, and 14.4 V for the 12 V batteries, which respectively correspond to the discharge-end cell potential for the burst of energy output, the discharge-end cell potential for the 5-h rate of discharge, and the charge-end cell potential typically determined for the 12 V lead-acid batteries. As clearly seen in Fig. 1, high-power output and input are possible in the wide range of the SOC of the cell. About 90% of the cell capacity can be used to supply the burst of energy for a short period of time until the cell potential reaches 7.2 V for the 12 V batteries, and the battery can be fully charged from any SOC.

Fig. 2 shows the selected charge and discharge curves of the LTO/LAMO cell operated at 2.27 mA cm^{-2} in cell potential ranging from 0 to 3.4 V for 250 cycles at −10 °C. The horizontal axis on the top of figure is given in mAh g^{-1} based on the weight of LTO and that at the bottom is given in mAh g^{-1} based on the weight of LAMO. The vertical axis at the right hand side is the calculated cell potential when the five LTO/LAMO cells are connected in series. The applied current corresponds to 100 mA g^{-1} based on the weight of LAMO, i.e., 1-h or 1 C rate. The charge and discharge curves observed at the 1st, 50th, 100th, 150th, 200th, and 250th cycles are shown in this figure. Rechargeable capacity observed at the first cycle is ca. 80 mAh g^{-1} based on the weight of LAMO and those observed at 50th to 250th cycle are ca. 72 mAh g^{-1}. The rechargeable capacity of the LTO/LAMO cell is invariable during the subsequent 200 cycles at −10 °C. Fig. 3 shows the charge and discharge curves of the LTO/LAMO cell operated at 25 °C before and after 250 cycles at −10 °C. The discharge capacities before and after are respectively 101 and 99 mAh g^{-1} based on the weight of LAMO, indicating that the loss of capacity is negligibly small. Although the first charge capacity at 25 °C after 250 cycles at −10 °C is 92 mAh g^{-1} based on the weight of LAMO, the rechargeable capacity is recovered for the subsequent cycles as seen in Fig. 3.

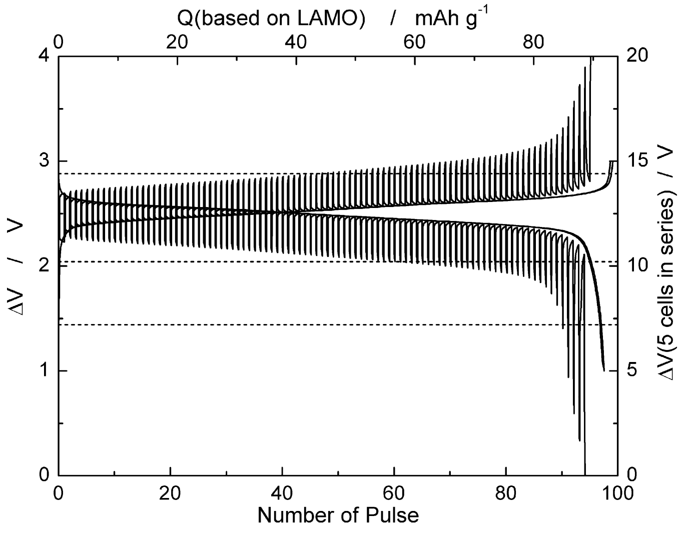

Fig. 1. Pulse charge and discharge curves of the LTO/LAMO cell operated at 15.3 mA cm^{-2} for 5 s current on and 25 s off at 25 °C. The current corresponds to 0.68 A g^{-1} based on the weight of LAMO and 1 A g^{-1} based on LTO. Continuous charge and discharge curves of the cell operated at 0.5 mA cm^{-2} are also shown. The positive-electrode mix is 51.3 mg with 144 μm thick and the negative-electrode mix is 34.8 mg with 135 μm.

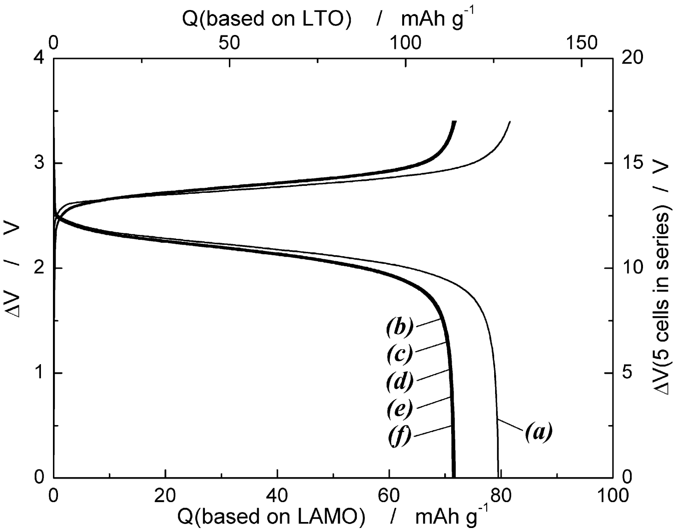

Fig. 2. Selected charge and discharge curves of the LTO/LAMO cell operated at 2.27 mA cm^{-2} in cell potential ranging from 0 to 3.4 V at −10 °C. The applied current corresponds to 100 mA g^{-1} based on the weight of LAMO, i.e., 1-h or 1 C rate. Charge and discharge curves observed at (a) 1st, (b) 50th, (c) 100th, (d) 150th, (e) 200th, and (f) 250th cycles are shown. The positive-electrode mix is 51.8 mg with 141 μm thick and the negative-electrode mix is 32.6 mg with 123 μm.

Fig. 4 shows the selected charge and discharge curves of the LTO/LAMO cell operated at 4.44 mA cm^{-2} in cell potential ranging from 0 to 3.4 V for 250 cycles at 25 °C. The applied current corresponds to 200 mA g^{-1} based on the weight of LAMO, i.e., 1/2-h

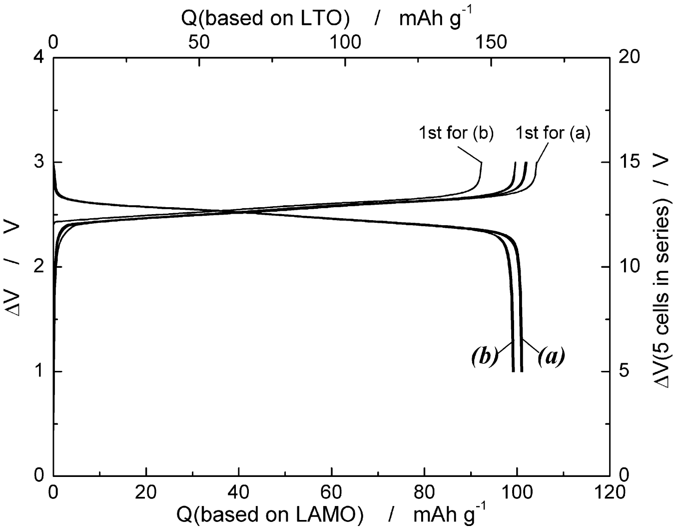

Fig. 3. Charge and discharge curves of the LTO/LAMO cell operated at 0.50 mA cm^{-2} in cell potential ranging from 1 to 3 V at 25 °C (a) before and (b) after the 250 cycles at −10 °C.